ENHANCING SILVER TARNISH-RESISTANCE

FIELD OF THE INVENTION

The present invention relates to the use of organo-sulphur compounds in the enhancement of the tarnish resistance of silver alloys, to silver articles of enhanced tarnish resistance that have been surface-treated with the organo-sulphur compounds and to methods of keeping and display of the treated articles. It also relates to a water-based composition that can be used for the treatment of a metal which may be a silver alloy but which may also be another metal requiring surface treatment to impart tarnish resistance e.g. copper, brass or nickel.

BACKGROUND TO THE INVENTION

Silver alloys and their tarnish-resistance

Standard Sterling silver provides manufacturers and silversmiths with a versatile and reliable material but it is inevitable that finished articles will require further cleaning and polishing to temporarily remove undesired tarnish products. It is well-known that with exposure to everyday atmospheric conditions, silver and silver alloys develop a lustre-destroying dark film known as tarnish.

Since ancient times it has been appreciated that unalloyed 'fine' silver is too soft to withstand normal usage, and it has been the practice to add a proportion of a base metal to increase hardness and strength. In the UK, legislation that has existed since the fourteenth century specifies a minimum silver content of articles for sale at 92.5% (the Sterling standard), but does not specify the base metal constituents. Experience convinced early silversmiths that copper was the most suitable of the metals available to them. Modern silver-sheet manufacturers generally adhere to this composition, although sometimes a proportion of copper is replaced by cadmium to attain even greater ductility.

Sterling with a 2.5% cadmium content is a standard material for spinning and stamping. Lower grades of silver alloys are common in many parts of Europe for the production of hollow-ware and cutlery. The 800-grade alloys (Ag parts per thousand) are predominantly used in southern and mid-Europe whereas in Scandinavia the 830 standard is predominant.

In all but the largest manufacturing companies, most of the annealing and soldering required to assemble finished or semi-finished articles is carried out with the flame of an air-gas blowtorch. The oxidising or reducing nature of the flame and the temperature of the articles are controlled only by the skill of the silversmith. Pure silver allows oxygen to pass easily through it, particularly when the silver is heated to above red heat. Silver does not oxidise in air, but the copper in a silver/copper alloy is oxidised to cuprous or cupric oxide. Pickling of the oxidised surface of the article in hot dilute sulphuric acid removes the superficial but not the deeper-seated copper oxide so that the surface consists of fine or unalloyed silver covering a layer of silver/copper oxide mixture. The pure silver is easily permeated during further heating, allowing copper located deeper below the surface to become oxidised. Successive annealing, cold working and pickling produces a surface that exhibits the pure lustre of silver when lightly polished but with heavier polishing reveals dark and disfiguring stains known as 'firestain' or 'fire'. Soldering operations are much more productive of deep firestain because of the higher temperatures involved. When the depth of the firestain exceeds about 0.025mm (0.010 inches) the alloy is additionally prone to cracking and difficult to solder because an oxide surface is not wetted by solder so that a proper metallurgical bond is not formed.

Patent GB-B-2255348 (Rateau, Albert and Johns; Metaleurop Recherche) disclosed a novel silver alloy that maintained the properties of hardness and lustre inherent in Ag-Cu alloys while reducing problems resulting from the tendency of the copper content to oxidise. The alloys were ternary Ag-Cu-Ge alloys containing at least 92.5 wt% Ag, 0.5-3 wt% Ge and the balance, apart from

impurities, copper. The alloys were stated to be stainless in ambient air during conventional production, transformation and finishing operations, to be easily deformable when cold, to be easily brazed and not to give rise to significant shrinkage on casting. They were also stated to exhibit superior ductility and tensile strength and to be annealable to a required hardness. Germanium was stated to exert a protective function that was responsible for the advantageous combination of properties exhibited by the new alloys, and was in solid solution in both the silver and the copper phases. The microstructure of the alloy was said to be constituted by two phases, a solid solution of germanium and copper in silver surrounded by a filamentous solid solution of germanium and silver and copper. The germanium in the copper-rich phase was said to inhibit surface oxidation of that phase by forming a thin GeO or GeO_2 protective coating which prevented the appearance of firestain during brazing and flame annealing which results from the oxidation of copper at high temperatures. Furthermore the development of tarnish was appreciably delayed by the addition of germanium, the surface turned slightly yellow rather than black and tarnish products were easily removed by ordinary tap water. The alloy was said to be useful *inter alia* in jewellery. However, the alloy disclosed in the above patent suffers limitations insofar as it can exhibit large grain size, leading to poor deformation properties and formation of large pools from low-melting eutectics resulting in localised surface melting when the alloy is subject to the heat of an air torch.

Patents US-A-6168071 and EP-B-0729398 (Johns) disclose a silver/germanium alloy which comprised a silver content of at least 77 wt % and a germanium content of between 0.4 and 7%, the remainder principally being copper apart from any impurities, which alloy contains elemental boron as a grain refiner at a concentration of more than 0ppm and less than 20ppm. The boron content of the alloy can be achieved by providing the boron in a master copper/boron alloy having 2 wt % elemental boron. It was reported that such low concentrations of boron surprisingly provide excellent grain refining in a silver/germanium alloy, imparting greater strength and ductility to the alloy

compared with a silver/germanium alloy without boron. The boron in the alloy inhibits grain growth even at temperatures used in the jewellery trade for soldering, and samples of the alloy were reported to have resisted pitting even upon heating repeatedly to temperatures where in conventional alloys the copper/germanium eutectic in the alloy would melt. Strong and aesthetically pleasing joints between separate elements of the alloy can be obtained without using a filler material between the free surfaces of the two elements and a butt or lap joint can be formed by a diffusion process or resistance or laser welding techniques. Compared to a weld in Sterling silver, a weld in the above-described alloy has a much smaller average grain size that improved the formability and ductility of the welds, and an 830 alloy has been welded by plasma welding and polished without the need for grinding.

Ternary and quaternary alloys e.g. Ag-Cu-Ge alloys and Ag-Cu-Zn-Ge alloys include two base metal alloying elements, Cu and Ge, in a noble parent metal, Ag. On exposure to an oxidising atmosphere, two oxidation reactions have to be considered. Firstly, the oxidation of copper to cuprous oxide:

$$4[Cu]_{alloy} + 0_2\,(g) \rightarrow 2Cu_20\,(s) \qquad (1)$$

Secondly, the oxidation of germanium to germanium (di)oxide:

$$[Ge]_{alloy} + 0_2\,(g) \rightarrow GeO_2\,(s) \qquad (2)$$

The above equation shows formation of germanium (IV) oxide, GeO_2, but there may also be formed germanium (II) oxide, GeO or an intermediate material Ge_xO_y where x is 1 and y is greater than 1 but less than 2. Under standard conditions, i.e. for pure Cu and pure Ge each reacting with pure oxygen gas at 1 atm pressure to form the pure oxide phase, both reactions are feasible, with the chemical driving force for reaction (2) being higher than that of reaction (1) by a factor of 1.65.

According to WO 02/095082 (Johns) tarnish resistance of ternary alloys of silver, copper and germanium or quaternary alloys of silver, copper, zinc and germanium can be increased by casting a molten mixture to form the alloy and

annealing the alloy to reduce its thickness and re-crystallize the grains in the alloy, the annealing being carried out under a selectively oxidizing atmosphere e.g H_2/H_2O or CO/CO_2 to promote the formation of GeO_2 while preventing the formation of Cu_2O.

Treatment compositions for removing or preventing silver tarnish

Various proposals have been made for cleaning or protecting Sterling silver and other known grades of silver to remove tarnish and/or to inhibit the formation of tarnish.

US-A-2841501 discloses a silver polish based on an abrasive powder and a C_{12}-C_{20} n-alkane thiol which is said to be non-toxic, to have a mild odor and to protect silver against tarnishing by forming a monomolecular layer R-S-Ag wherein R represents the alkane chain of the thiol, said layer forming a physical barrier between the silver and reactive ingredients of the atmosphere.

GB-A-1130540 is concerned with the protection of a finished surface of Sterling or Britannia silver as a step in a production run, and discloses a process that comprises the steps of:

wetting a clean silver surface of an article with a solution comprising 99 parts by weight of a volatile organic solvent, for example trichloroethylene or 1,1,1-trichloroethane and from 0.1-1.8 parts by weight of an organic solute containing a –SH group and capable of forming a transparent colourless protective layer on the silver surface, for example stearyl and cetyl mercaptan or thioglycollate;

allowing the solution to react with the surface to form such a layer and allowing the solvent to evaporate; and

washing the surface with a detergent solution, rinsing the surface with hot water and allowing it to dry. The above process is stated to provide a "long-term finish" intended to last the intended shelf-life until the article reaches the user.

Halohydrocarbons were said to be the most suitable solvents but their suitability on environmental grounds is now open to question. Ethers were said to be flammable and toxic, and lower alcohols were said to be poor solvents. Water is not mentioned as a solvent. Applicants have seen a report on the Internet from ATOFINA Chemicals Inc that the solubility of mercaptans in water decreases progressively from 23.30 g/litre for methyl mercaptan to 0.00115 g/litre for nonyl mercaptan, and data for for both hexadecyl and octadecyl mercaptan (CAS 2885-00-9) reports them as water- insoluble.

US-A-6183815 (Enick) also teaches that treatments of the above kind are result in the formation of a self-assembled coating derived from the thiol compounds in which the sulphur atoms are bound onto the metal surface and the alkyl tails are directed away from the metal surface. In the examples of that specification, fluoroalkyl amides e.g. $CF_3(CF_2)_5CONH(CH_2)_2SH$ in aqueous alcohols e.g. aqueous isopropanol are sprayed onto the surface of silver, after which the surface is rinsed and dried with a soft cloth. The fluoroalkyl amides lack detectable odour and can dissolve in lower alcohols or alcohol/water mixtures, although it is apparent from the description and examples that not all alcoholic solvents produce good films.

Yousong Kim *et al* report that the adsorption of thiols onto silver proceeds through an anodic oxidation reaction that produces a shift of the open circuit potential of the substrate metal in the negative direction or if the potential is fixed an anodic current peak:

$RSH + M(0) \rightarrow RS\text{-}M(I) + H^+ + e^-(M)$ (M = Au or Ag), see *http://www.electrochem.org/meetings/past/200/abstracts/symposia/h1/1026.pdf*

Kwan Kim, *Adsorption and Reaction of Thiols and Sulfides on Noble Metals*, Raman SRS-2000, 14-17 August 2000, Xaimen, Fujian, China, http://pcoss.org/icorsxm/paper/kuankim.pdf , also discloses the formation of self-assembled monolayers and discloses that alkanethiols, dialkyl sulfides and dialkyl

disulfides self-assemble on silver surfaces with aliphatic dithiols forming dithoiolates by forming two Ag-S bonds.

In contrast, the literature on formation of alkylthiols of germanium is relatively sparse. The dissociative adsorption of H_2S at a Ge 100 surface to yield adsorbed –SH groups and adsorbed hydrides has been reported by Nelen *et al.*, *Applied Surface Science,* **150,** 65-72 (1999), see http://www.chem.missouri.edu/Greenlief/pubs/00005797.pdf, see also a report by Professor Michael Greenlief of the University of Missouri-Columbia http://www.chem.missouri.edu/Greenlief/Research.html that room temperature exposure of H_2S to Ge(100) results in dissociative adsorption that can be followed easily by ultraviolet photoelectron spectroscopy. The reaction of alkanethiols with Ge to form a high quality monolayer has been reported in the context of semiconductor and nanotechnology by Han *et al*, *J. Am. Chem. Soc.*, **123**, 2422 (2001). In the experiment described, a Ge(111) wafer is sonicated in acetone to dissolve organic contaminants and immersed in concentrated HF to remove residual oxide and produce a hydrogen-terminated surface, after which the wafer is immersed in an alkanethiol solution in isopropanol, sonicated in propanol and dried.

SUMMARY OF THE INVENTION

Although GB-A-1130540 was alleged to provide a long-term finish, the experience of one of the inventors who is a silversmith is this type of treatment does not fully solve the difficulties created by tarnish in the period between manufacture and supply to the ultimate purchaser or user and suffers from a number of shortcomings. Although a silver product might arrive at the retailer in an untarnished state, it was largely the result of the wrapping applied by the manufacturer, which protected the article from air. Once the wrapping was removed and the article was displayed in a retail environment such as a display case in a hotel where it was subject to ambient air and the heat of artificial

lighting, an article of conventional Sterling silver would require re-polishing after one week and after two weeks would normally be so tarnished as to be unsaleable. At an exhibition, the life of an article on display before significant tarnish sets in may be as short as 3-4 days. Re-polishing produces wear and fine handling scratches, so that unless the article can be sold quickly it looses its pristine appearance. The need to polish display silver at frequent intervals adds to the labour cost of a jeweller or other retail establishment, whose management take the view that its staff should be employed to sell products and not to clean stock. Tarnish at point of sale or display is therefore a serious problem that reduces the willingness of those in the distribution chain to stock and display silver products, and which has not yet been adequately solved.

When the product reaches the ultimate purchaser, it is of course desirable that the task of tarnish removal should be made as infrequent and undemanding as possible.

Silver alloys according to the teaching of GB-B-2255348 and EP-B-0729398 are now commercially available in Europe and in the USA under the trade mark Argentium, and the word "Argentium" as used herein refers to these alloys. Although they exhibit improved tarnish resistance compared to e.g. Sterling silver, and any tarnish that forms can be removed by simple washing, there is still room for improvement in tarnish resistance. That remains true even when annealing is conducted in a selectively oxidising atmosphere as disclosed in WO 02/095082.

It has now been found that an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide can be used for the surface treatment of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing so as to reduce or further reduce tarnishing of the alloy such that a sample can be subjected to hydrogen sulphide gas above a 20% solution of

ammonium polysulphide for at least 30 minutes and typically 45-60 minutes at room temperature while retaining a generally untarnished appearance.

The invention also therefore relates to the use of an organic compound containing –SH or –S-S- bonds e.g. a C_2-C_{40} (preferably C_{12}-C_{24}) alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide in the preparation of a tarnish inhibitor for an article of a silver/germanium alloy that has a silver content of at least 77 wt % and a germanium content of between 0.1 and 7% so as to reduce tarnishing of said alloy such that a sample can be supported close above a 20% solution of ammonium polysulphide for at least 30 minutes and typically 45-60 minutes while retaining a generally untarnished appearance.

The invention further provides an alloy of silver, or a shaped article formed of said alloy, containing an amount of germanium that is effective to reduce firestain and/or tarnishing and that has been treated with a C_{12}-C_{24} alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide.

The invention further provides a method for manufacturing a tarnish-resistant silver article, which comprises the steps of:

forming a shaped article of an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing;

surface treating the article with an alkanethiol, alkyl thioglycollate, dialkyl sulphide or dialkyl disulphide; and

introducing the article into packaging.

The above accelerated tarnish test in which the article is subject to hydrogen sulphide gas from the ammonium polysulphide solution above which it is suspended at a height of e.g. 30mm corresponds to a period of a year or more in a retail environment where an article is on display and exposed to ambient atmosphere and may be subject to elevated temperatures. It is the combination of the protective function of the germanium content of the alloy with the further

protection from the organo-sulphur compound that is believed to be responsible for the observed increase in tarnish resistance. The period during which the article retains its untarnished appearance under these severe conditions may be three or more times the corresponding period for an article that has not been treated with an organo-sulphur compound, which is unexpected because the same accelerated tarnish test carried out under the same conditions on a conventional Sterling silver article not containing protective germanium does not reveal a significant increase in untarnished lifetime between its untreated and organo-sulfur treated states. Accelerated tarnishing trials carried out using Argentium and standard Sterling silver samples immersed in solutions of octadecyl mercaptan and hexadecyl mercaptan have shown that the protective thiol is removed from the standard Sterling sample but not from the Argentium silver samples on rubbing with a tissue soaked in a solvent (EnSolv 765, an n-propyl bromide based solvent cleaner discussed below). In accelerated testing the solvent-rubbed regions of standard Sterling silver discolour more rapidly than the un-rubbed regions whereas in Argentium silver no noticeable difference in appearence develops between the rubbed and un-rubbed regions, suggesting that thiol bonding is stronger or more effective.

Accelerated tarnishing tests with Argentium Sterling using ammonium polysulphide have been reported by the Society of American Silversmiths, see

http://www.silversmithing.com/1argentium4.htm

and in a comparative test the Argentium Sterling remained untarnished after one hour whereas conventional Sterling became tarnished after less than 15 minutes. However, in this test 0.5ml of 20% ammonium polysulfide solution is mixed with 200ml of distilled water, so that the test is greatly less severe than when samples are exposed to the 20% solution itself. In WO 02/095082, samples were suspended above 20% ammonium polysulphide, but the exposure times were relatively short, and onset of yellowing was reported for Ag-Cu-Ge alloys after 3-5 minutes exposure. Other tests reported in that specification involve placing

samples in a desiccator containing flowers of sulphur and calcium nitrate and are less severe than the ammonium polysulphide test.

As part of their program for developing improved formulations for the treatment agents described above, the applicants have unexpectedly discovered that the treatment agents can be dissolved or dispersed directly in aqueous surfactant without the need for preliminary dissolving of the treatment agent in an organic solvent and subsequent mixing of the resulting solution with aqueous liquid. Embodiments of the above compositions are optically clear and storage-stable at ambient temperatures for a period of weeks or months. The treatment composition may therefore be water-based and comprise an alkanethiol, alkyl thioglycollate, dialkyl sulfide or dialkyl disulfide and a mixture of an anionic surfactant with a neutral or amphoteric surfactant and water.

DETAILED DESCRIPTION OF THE INVENTION

Silver-copper-germanium alloys

The alloys that may be treated according to the invention include an alloy of silver containing an amount of germanium that is effective to reduce firestain and/or tarnishing. US-A-6406664 (Diamond) discloses that amounts of germanium as low as 0.1wt% can be effective provided that substantial amounts of tin are present but although formulation examples are given, no test data for corrosion or firestain is given either for articles made by casting or for articles fabricated from sheet. The inventor considers that 0.5 wt% Ge provides a preferred and more realistic lower limit and that in practice use of less than 1wt% is undesirable. A two-component copper-free alloy could comprise 99% Ag and 1 % Ge, and a tarnish-free casting alloy for jewellery has been reported that comprises 2.5%Pt, 1% Ge, balance Ag and optionally containing Zr, Si or Sn.

The ternary Ag-Cu-Ge alloys and quaternary Ag-Cu-Zn-Ge alloys that can suitably be treated by the method of the present invention are those having a silver content of at least 30%, preferably at least 60%, more preferably at least 80%, and most preferably at least 92.5%, by weight of the alloy, up to a maximum of no more than 98%, preferably no more than 97%. The germanium content of the Ag-Cu-(Zn)-Ge alloys should be at least 0.1%, preferably at least 0.5%, more preferably at least 1.1%, and most preferably at least 1.5%, by weight of the alloy, up to a maximum of preferably no more than 6.5%, more preferably no more than 4%.

If desired, the germanium content may be substituted, in part, by one or more elements which have an oxidation potential selected from Al, Ba, Be, Cd, Co, Cr, Er, Ga, In, Mg, Mn, Ni, Pb, Pd, Pt, Si, Sn, Ti, V, Y, Yb and Zr, provided the effect of germanium in terms of providing firestain and tarnish resistance is not unduly adversely affected. The weight ratio of germanium to substitutable

elements may range from 100: 0 to 60: 40, preferably from 100: 0 to 80: 20. Preferably, the germanium content consist entirely of germanium, i. e. the weight ratio is 100: 0.

The remainder of the ternary Ag-Cu-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper, which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy. For an '800 grade' ternary alloy, for example, a copper content of 18.5% is suitable. The remainder of the quaternary Ag-Cu-Zn-Ge alloys, apart from impurities and any grain refiner, will be constituted by copper which should be present in an amount of at least 0.5%, preferably at least 1%, more preferably at least 2%, and most preferably at least 4%, by weight of the alloy, and zinc which should be present in a ratio, by weight, to the copper of no more than 1: 1. Therefore, zinc is optionally present in the silver-copper alloys in an amount of from 0 to 100 % by weight of the copper content. For an '800 grade' quaternary alloy, for example, a copper content of 10.5% and zinc content of 8% is suitable.

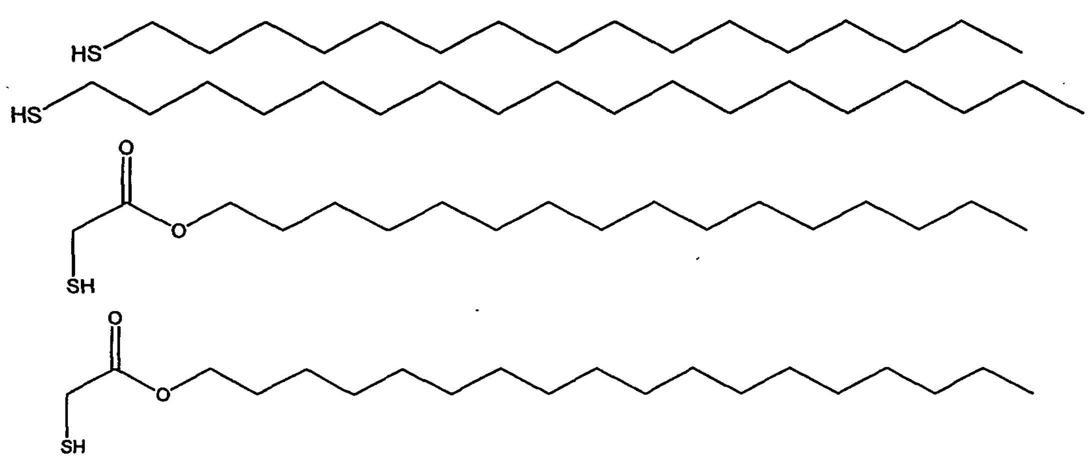
In addition to silver, copper and germanium, and optionally zinc, the alloys preferably contain a grain refiner to inhibit grain growth during processing of the alloy. Suitable grain refiners include boron, iridium, iron and nickel, with boron being particularly preferred. The grain refiner, preferably boron, may be present in the Ag-Cu-(Zn)-Ge alloys in the range from 1 ppm to 100 ppm, preferably from 2 ppm to 50 ppm, more preferably from 4 ppm to 20 ppm, by weight of the alloy.

In a preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and any grain refiner, of 80% to 96% silver, 0.1 % to 5% germanium and 1 % to 19.9% copper, by weight of the alloy. In a more preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 98% silver, 0.3% to 3% germanium and 1% to 7.2%

copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner. In a further preferred embodiment, the alloy is a ternary alloy consisting, apart from impurities and grain refiner, of 92.5% to 96% silver, 0. 5% to 2% germanium, and 1% to 7% copper, by weight of the alloy, together with 1 ppm to 40 ppm boron as grain refiner.

Protective agents

As protective agent there may be used a compound containing a long chain alkyl group and a –SH or –S-S- group, e.g. an alkanethiol, dialkyl sulfide or dialkyl disulfides in which the chain is preferably at least 10 carbon atoms long and may be C_{12}-C_{24}. The –SH or –S-S- compounds that many be used include straight chain saturated aliphatic compounds containing 16-24 carbon atoms in the chain, for example cetyl mercaptan (hexadecyl mercaptan) and stearyl mercaptan (octadecyl mercaptan) and cetyl and stearyl thioglycollates whose formulae appear below.



Octadecyl mercaptan is a white to pale yellow waxy solid that is insoluble in water and that melts at 15-16°C. Hexadecyl mercaptan is also a white or pale yellow waxy solid that melts at 30°C.

Formulations based on organic solvents

The protective agent may be used in solution in a solvent e.g. a non-polar organic solvent such as an alcohol e.g. methyl or ethyl alcohol, a ketone e.g. acetone or methyl ethyl ketone, an ether e.g. diethyl ether, an ester e.g. n-butyl acetate, a hydrocarbon, a halocarbon e.g. methylene chloride, 1,1,1-trichloroethane, trichloroethylene, perchloroethylene or HCFC 141b. The protective agent may comprise 0.1-1 wt% of the solvent. Solvents based on alkyl or aryl halides may be used e.g. *n*-propyl bromide which is presently preferred on the ground of the short atmospheric life of that compound, its relatively low toxicity compared to other halocarbons, its favourable chemical and physical properties and its boiling point, specific heat and latent heat of vaporization.

US-A-5616549 discloses a solvent mixture comprising: 90 percent to about 96.5 percent *n*-propyl bromide; 0 percent to about 6.5 percent of a mixture of terpenes, the terpene mixture comprising 35 percent to about 50 percent cis-pinane and 35 percent to about 50 percent trans-pinane; and 3.5 percent to about 5 percent of a mixture of low boiling solvents, the low boiling solvent mixture comprising 0.5 percent to 1 percent nitromethane, 0.5 percent to 1 percent 1,2-butylene oxide and 2.5 percent to 3 percent 1,3-dioxolane. The solvent mixture has the following advantages:

(i) it is properly stabilized against any free acid that might result from oxidation of the mixture in the presence of air, from hydrolysis of the mixture in the presence of water, and from pyrolysis of the mixture under the influence of high temperatures;

(ii) it is non-flammable and non-corrosive;

(iii) the various components of the solvent mixture are not regulated by the U.S. Clean Air Act; and

(iv) none of the various components of the solvent mixture are known cancer causing agents (i.e., the various components are not listed by N.T.I., I.A.R.C. and California Proposition 65, nor are they regulated by OSHA).

Moreover, the solvent mixture has a high solvency with a kauri-butanol value above 120 and, more preferably, above 125. In addition, the solvent mixture has an evaporation rate of at least 0.96 where 1,1,1-Trichloroethane=1. Upon evaporation, the solvent mixture leaves a non-volatile residue (NVR) of less than 2.5 mg and, more preferably, no residue. Solvents made in accordance with the above patent are available from Enviro-Tech International, Inc of Melrose Park, Illinois, USA under the trade name EnSolv.

Formulations based on organic solvent and water

For many purposes, e.g. light industrial applications, it may be preferred to carry out the anti-tarnish treatment using a predominantly aqueous solvent system. For this purpose, the protective agent may be dissolved in a water-immiscible organic solvent, for example a solvent based on *n*-propyl bromide, the resulting solution may be mixed with a relatively concentrated water-based soap or detergent composition which acts as a "carrier", after which water is added to the resulting mixture to provide an aqueous treatment dip or combined degreasing and treatment solution. Thus an aqueous dip has the advantages that a solvent degreasing system is not necessary, the dip is easily made and may be used cold, all areas of immersed articles can come into contact with the stearyl mercaptan or other treatment agent, Argentium Silver only requires 2 minutes – 1 hour in the dip, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, and the dip can be easily used in a manufacturing environment before articles are sent to retailers.

Preferred water-based detergents may be based on anionic, alkoxylated non-ionic or water-soluble cationic surface active agents or mixtures of them and preferably have a pH at or close to 7. Anionic surfactants may be based on alkyl sulphates and alkyl benzene sulphonates, whose harshness on prolonged skin exposure may be reduced by the co-presence or use of alkyl ethoxy sulphates (US-A-3793233, Rose *et al.*; 4024078 Gilbert; 4316824 Pancherni). Other known

surfactants e.g. betaines may also be present, see e.g. US-A-4555360 (Bissett). A suitable formulation containing 5-15 wt% non-ionic surfactants and 15-30 wt% anionic surfactants is available commercially in the UK under the trade name Fairy Liquid (Proctor & Gamble).

An aqueous liquid may also be made by dissolving the treatment agent in a non-organic solvent and adding a relatively concentrated aqueous detergent liquid, for example undiluted Fairy Liquid. This provides a detergent liquid that has a number of advantages: the soapy liquid is easily made, the liquid is easily applied to the Argentium Silver articles with a damp sponge/cotton wool/cloth etc, the liquid and lather enables the stearyl mercaptan or other treatment agent to get into those awkward areas on an article where a cloth may not be able to reach, rinsing and drying of articles are made easy as water droplets are repelled from the surface of the polished silver, the process can be easily used in a manufacturing environment before articles are sent to retailers and can also be easily used in a retail or domestic environment. Furthermore, the hydrophobic properties imparted to silver/silver alloy on treatment with the present thiol-based treatment agents may alleviate or overcome the problems of water-marks or water-staining from rinsing processes in a manufacturing or domestic environment.

Formulations based on aqueous liquids

It has surprisingly been found that formulations containing effective amounts of the treatment agents can be made by dissolving them directly in aqueous liquids containing an anionic and a neutral or amphoteric surfactant and free from water-immiscible organic solvents and preferably free from all other solvents. The treatment agents may be dissolved in relatively concentrated surfactant-containing aqueous liquids, which may be used as such or after subsequent dilution with water, see in particular the instructions given in the preceding section.

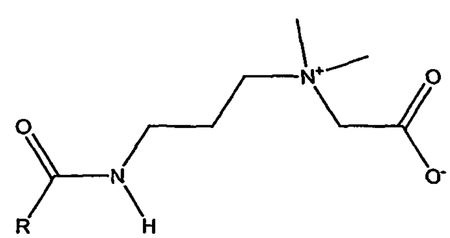
The treatment agent may be present in said composition, prior to dilutiuon thereof, in an amount of at least 0.1 wt % and preferably at least 1 wt %, the solids content of the composition being at least 5 wt %, typically 10-40 wt % and possibly 50 wt% or more. The ability of aqueous surfactant liquids to dissolve or disperse such relatively high concentrations of higher alkyl thiols and other treatment agents which are reported to be highly water-insoluble has not been described. The resulting concentrates may be diluted with water to provide an aqueous treatment dip or combined degreasing solution and dip for use as explained above, and it has been found that the treatment agent may remain in solution or suspension following such dilution and may remain effective for the surface treatment of silver-copper or silver-copper-germanium alloys and possibly other metals such as copper, brass and nickel where surface protection films may retard corrosion. Particularly good results from the stability and effectiveness standpoint may be obtained by mixing hexadecyl mercaptan (in the liquid state) straight into a surfactant "carrier" and using the solution as such or on subsequent dilution with water.

In particular, the present treatment agents can be successfully dispersed in aqueous liquids containing mixtures of neutral and anionic surfactants with the neutral surfactants providing e.g. about 33 wt% of the total surfactant present. Treatment agents that can be dispersed in such agents include n-hexadecyl thiol and n-octadecyl thiol. They can also be successfully dispersed in aqueous liquids containing mixtures of amphoteric or zwiterionic surfactants and anionic surfactants and such mixtures can provide relatively storage stable optically clear solutions with little or no tendency to re-precipitate the treatment agent. In that case the weight ratio of the amphoteric or zwitterionic surfactant to the anionic surfactant may be from 1:10 to 10:1, typically close to 1:3.

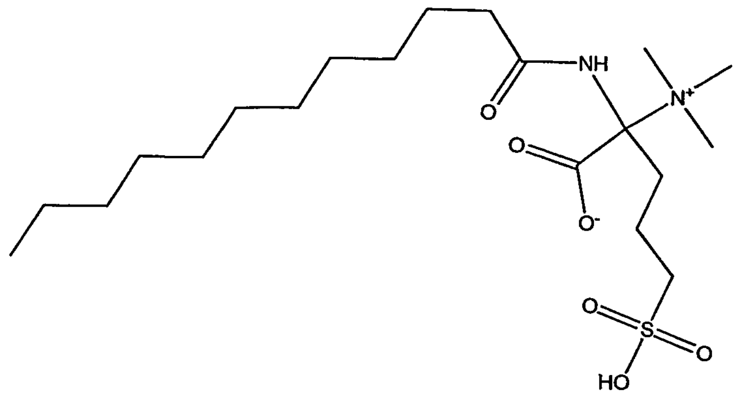
Amphoteric or zwitterionic surfactants that may be used alone or in admixture with one another and/or with nonionic surfactants and/or with anionic surfactants may be derivatives of secondary or tertiary amines, derivatives of

heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. The cationic atom in the quaternary compound can be part of a heterocyclic ring. In all of these compounds there is at least one aliphatic group, straight chain or branched, containing from about 3 to 18 carbon atoms and at least one aliphatic substituent containing an anionic water-solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

Examples of zwitterionic surfactants that may be employed include betaine surfactants, which are preferred, imidazoline-based surfactants, aminoalkanoate surfactants and iminodialkanoate surfactants. Suitable such surfactants include amidocarboxybetaines, such as cocoamidodimethylcarboxymethylbetaine, laurylamidodimethylcarboxymethyl-betaine, cetylamidodimethylcarboxy-methylbetaine, and cocoamido-bis-(2-hydroxyethyl)carboxymethyl-betaine. Particularly preferred are amidocarboxybetaines betaines of the formula below wherein R represents C_8-C_{18} alkyl e.g. cocamidopropyl betaine. That compound is generally regarded as safe: in an Ames test conducted by BASF it did not prove mutagenic to Salmonella indicator organisms and in a human repeated patch insult test (HRIPT) it did not indicate either contact hypersensitivity or photoallergy (see the MAFO CAB cocamidopropyl amino betaine data sheet published by BASF):



Also useful are sulphobetaine surfactants, e.g amido sulfobetaines such as lauramido-sulfopropylbetaine of formula indicated below,



cocamido-2-hydroxypropylsulfobetaine, cocoamidodimethylsulfopropyl-betaine, stearylamido-dimethylsulfopropylbetaine, and laurylamido-bis-(2-hydroxyethyl)-sulfopropylbetaine. Also useful may be imidazoline-based surfactants including gylcinate and amphoacetate compounds e.g. cocoamphocarboxypropionate, cocoamphocarboxypropionic acid, cocoamphocarboxyglycinate, and cocoamphoacetate, aminoalkanoate surfactants e.g. n-alkylamino-propionates and n-alkyliminodipropionates such as N-lauryl-β-amino propionic acid and salts thereof, and N-lauryl-β-imino-dipropionic acid and salts thereof.

Non-ionic surface-active agents that may be used alone or in admixture include compounds produced by the condensation of an alkylene oxide with an organic hydrophobic compound that may be aliphatic or alkyl aromatic. The length of the hydrophilic or polyoxyalkylene moiety that is condensed with any particular hydrophobic compound can be adjusted to yield a water-soluble compound having the desired balance between hydrophilic and hydrophobic moieties. Semi-polar nonionic surface active agents may also be used, including amine oxides, phosphine oxides, and sulfoxides. Suitable classes of compound include:

- Polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight or branched chain, with ethylene oxide, the said ethylene oxide being present in amounts equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in

such compounds may be derived, for example, from polymerized propylene, diisobutylene, octene, or nonene.

- Condensation products of aliphatic alcohols with ethylene oxide. The alkyl chain of the aliphatic alcohol may either be straight or branched and generally contains from about 8 to about 22 carbon atoms.
- Condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine.
- Amine oxide surfactants, for example dimethyldodecylamine oxide, dimethyltetradecylamine oxide, ethylmethyltetradecylamine oxide, cetyldimethylamine oxide, dimethylstearylamine oxide, cetylethylpropylamine oxide, diethyldodecylamine oxide, diethyltetradecylamine oxide, dipropyldodecylamine oxide, bis-(2-hydroxyethyl)dodecylamine oxide, bis-(2-hydroxyethyl)-3-dodecoxy-2-hydroxypropylamine oxide, (2-hydroxypropyl)methyltetradecylamine oxide, dimethyloleylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, and the corresponding decyl, hexadecyl and octadecyl homologs of the above compounds.
- Phosphine oxide surfactants, e.g. dimethyldodecylphosphine oxide, dimethyltetradecylphosphine oxide, ethylmethyltetradecylphosphine oxide, cetyldimethylphosphine oxide, dimethylstearylphosphine oxide, cetylethylpropylphosphine oxide, diethyldodecylphosphine oxide, diethyltetradecylphosphine oxide, dipropyldodecylphosphine oxide, dipropyldodecylphosphine oxide, bis-(hydroxymethyl)dodecylphosphine oxide, bis-(2-hydroxyethyl)dodecylphosphine oxide, (2-hydroxypropyl)methyltetradecylphosphine oxide, dimethyloleylphosphine oxide, and dimethyl-(2-hydroxydodecyl)phosphine oxide and the corresponding decyl, hexadecyl, and octadecyl homologs of the above compounds.
- Sulfoxide surfactants, for example octadecyl methyl sulfoxide, dodecyl methyl sulfoxide, tetradecyl methyl sulfoxide, 3-hydroxytridecyl methyl sulfoxide, 3-methoxytridecyl methyl sulfoxide, 3-hydroxy-4-dodecoxybutyl

methyl sulfoxide, octadecyl 2-hydroxyethyl sulfoxide, and dodecylethyl sulfoxide.

- Ethanolamide-based surfactants e.g. coconut fatty acid monoethanolamide or diethanolamide.

wherein R represents C_{10}-C_{40}, esp C_{12}-C_{18} alkyl e.g. oleyl- or coco-. Further surfactants may be based on diethylene triamine (DETA)-based quaternaries, such as diamidoamine ethoxylates and imidazolines, and esterquats. As a class, esterquats can be based on compounds including methyl diethanolamine (MDEA), triethanolamine (TEA), and N,N-dimethyl-3aminopropane-1,2-diol (DMAPD).

A wide variety of alkyl sulfates may bé used as anionic surface-active agents including fatty alcohol sulphates, fatty alcohol ether sulphates, alkyl phenol ether sulphates, alkyl aryl sulphonic acids and salts thereof , cumene, toluene and xylene sulphonates and salts thereof and alkyl sulphosuccinates e.g. sodium or ammonium lauryl sulfate. However, a preferred class of anionic surface active agents is polyol monoalkylether sulfates of the formula RO-$(CH_2CH_2)_nSO_3M$ wherein R represents C_{10}-C_{18} alkyl, n is 2-6 (preferably about 2-3) and M represents a monovalent cation. Such compounds are sulfonated ethoxylated C_{10}-C_{18} alkohols which may be derived from coconut oil or tallow or may be synthetic. Sodium laureth sulfate which has been used successfully herein is a sodium lauryl ether sulphate ethoxylated to an average of two moles of ethylene oxide per mole of lauric acid and sulfated, and is of formula $CH_3(CH_2)_{10}CH_2(OCH_2CH_2)_2OSO_3Na$.

In addition to simple treatment agents, the above compositions may be formulated into metal polishes e.g. for silver or brass. Such products may be formulated as liquid products into which objects such as jewellery or cutlery are to be dipped. After dipping, the objects are usually rinsed under water and dried

with a soft cloth. Alternative formulations take the form of creams or paptes which are applied with a soft cloth and then removed.

For formulation into dipping compositions, the active ingredients are normally an acid having a pKa of not more than 5, e.g. phosphoric, citric, oxalic, or tartaric acid together with thiourea or a derivative thereof e.g. an alkyl derivative such as methyl or ethyl thiourea. For formulation into creams or pastes there may be e.g. about 25 wt% of a mild abrasive such as precipitated chalk, infusorial earth, silica or γ-alumina (e.g. 0.05 μm grade). These ingredients are believed compatible with the surfactants and treatment agents and can be incorporated when convenient by simple mixing.

Treatment procedures

The surface treatment may be carried out after the manufacturing stages for a shaped article made of the alloy have been completed. The article may be of flatware, hollowware or jewellery. Fabrication steps may include spinning, pressing, forging, casting, chasing, hammering from sheet, planishing, joining by soldering brazing or welding, annealing and polishing using buffs/mops and aluminium oxide or rouge.

An article to be treated may be de-greased by various methods:

- Vapour degreasing with or without ultrasonics
- Aqueous degreasing with or without ultrasonics
- Organic solvent degreasing with or without ultrasonics (e.g. degreasing with ethanol or acetone prior to thiol treatment which may provide very good accelerated tarnish test results).
- Simultaneous degreasing and thiol treatment, the thiol being present in an organic or aqueous degreasing medium.

For example, the article may be degreased ultrasonically in a treatment bath, dipped into a bath containing the treatment agent e.g. 1 wt% stearyl mercaptan in solvent e.g. EnSolv, rinsed in one or more baths of the solvent and allowed to dry by evaporation. Rinsing excess thiol away with the same solvent that is used for thiol treatment is preferred, so that thiols that have not reacted with the metallic surface are removed and are unavailable to react with anything else. The solvent should leave no or substantially no residue, so that subsequent washing with water or aqueous solvents should be unnecessary and the article can be allowed to dry. The article may then be packed for delivery into the distribution chain. This may include wrapping the article in one or more protective sheets, placing it in a presentation box, and wrapping the presentation box in a protective wrapping e.g. of heat-shrunk plastics film. Articles which have been treated with an organic compound containing –SH or –S-S- groups as aforesaid and packaged should not only reach their point of sale in good condition but should if displayed e.g. on a shelf or in a cabinet for an extended period, expected to be at least 6 months and possibly 12 months or more, remain without development of significant tarnish.

The articles may alternatively simply be polished with a polish containing 1-5wt% of the organo-sulphur compound e.g. stearyl mercaptan together surfactants and a cleaning agent e.g. diatomaceous earth in a solvent. As a further alternative, they may be simply polished with a cloth impregnated with the sogano-sulphur compound e.g. cetyl or stearyl mercaptan e.g by impregnation with a treatment agent in an organic solvent e.g. n-propyl bromide followed by drying. The advantages of a cleaning cloth are that it is easily manufactured, can be easily used in a retail or domestic environment and is good for general upkeep of Argentium Silver (if required).

The treatment method of the invention would find particular benefit in the tarnish protection of blanks for stamping coins immediately before the stamping operation because it has been found that embodiments of the present films can

largely or wholly survive the stamping operation and can provide pritection against tarnishing for the newly minted coins. It will be appreciated that coins in mint condition are packaged for collectors with minimal handling, and that every ocasion of handling e.g. polishing with a soft cloth involves risk of damage to the coin. The risk of such damage is reduced by the present treatment which can impart prolonged tarnish resistance.

The invention will now be further described, by way of illustration only, with reference to the following examples. Throughout the examples, the term "enhanced tarnish resistance" of samples treated with stearyl mercaptan refers to the comparison with samples of Argentium Silver which have not had any treatment except for polishing and degreasing.

Example 1

Solvent dip application (solvent degreased samples)

Solutions were made up containing stearyl mercaptan (0.1, 0.5 and 1.0 gram) in EnSolv 765 (100 ml). Samples of Argentium Sterling which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes were each immersed in one of the stearyl mercaptan solutions for periods of 2 minutes, 5 minutes and 15 minutes. The samples were then buffed with clean cotton wool.

In order to evaluate tarnish resistance, the alloy samples were supported on a glass slide in a fume cupboard about 25mm above the surface of 20% ammonium polysulphide solution so as to be exposed to the hydrogen sulphide that arises from that solution. All of the samples demonstrated good tarnish resistance during a one-hour test, with very slight yellowing after 45 minutes exposure to the hydrogen sulphide. The light film on the samples was easily removed with a cleaning cloth impregnated with stearyl mercaptan.

By way of comparison, a standard Sterling silver sample started to discolour as soon as it was subjected to the above test and after one hour had formed a heavy black tarnish which could not be removed with a cleaning cloth impregnated with stearyl mercaptan. The results obtained with a second Sterling silver sample that had been wiped with the cleaning cloth were similar and discoloration started as soon as the sample had been placed into the test. An Argentium Sterling alloy produced in accordance with EP-B-0729398 showed onset of tarnishing after 3 minutes. Another sample of the Argentium Sterling alloy that had been annealed in a selectively oxidizing atmosphere as disclosed in WO 02/09502 showed onset of tarnishing after 6 minutes. The markedly increased delay in onset of tarnishing was unexpected in the absence of an increased delay in the case of the standard Sterling Silver article.

Example 2

Effect of post-treatment solvent cleaning

Example 1 was repeated for the Argentium samples except that instead of buffing with cotton wool after the mercaptan treatment, the samples were ultrasonically degreased in EnSolv 765 for 2 minutes. The samples were then tarnish tested as described in Example 1 and all found to show enhanced tarnish resistance. The ability of the protective effect of the stearyl mercaptan treatment to survive ultrasonic cleaning in EnSolv suggests that the tarnish resistance is being achieved by a surface reaction involving the stearyl mercaptan and possibly the germanium in the Argentium Silver, and not by formation of a grease or oil layer on the surface of the Argentium.

Example 3

Aqueous dip application (solvent degreased samples)

An anti-tarnish treatment solution was prepared using the following ingredients:

Stearyl mercaptan	1g
EnSolv 765	5 ml
Detergent (Fairy Liquid)	40 ml
De-ionised water	100 ml

The Stearyl Mercaptan was dissolved into the EnSolv 765 after which the resulting solution was mixed with detergent (Fairy Liquid) and diluted with water to provide an aqueous dip. Samples of Argentium silver were polished and ultrasonically degreased in EnSolv 765 for 2 minutes, immersed into the above aqueous dip for 2 minutes at ambient temperatures and then rinsed under running

tap water It was noted the water was immediately repelled from the polished surface, which left the samples dry. Samples were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance.

Example 4

Aqueous dip application 2 (detergent degreased samples)

Samples of Argentium Sterling were degreased in a 2% aqueous solution of a detergent (Fairy Liquid) and were then immersed in the treatment solution of Example 3. It was noted that the treated samples had become water-repellent as described in Example 3. Samples were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance. The above test was repeated except that the Fairy liquid in the treatment solution was replaced by a liquid hand soap (40 ml). When exposed to ammonium polysulphide solution, the samples did not show enhanced tarnish resistance. It is possible that this may have been because the hand soap was more dilute.

Example 5

Simultaneous degreasing and anti-tarnish treatment

The following solutions were prepared:-

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 20ml detergent (Fairy Liquid)
- 100ml de-ionised water

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765

- 30ml detergent (Fairy Liquid)
- 100ml de-ionised water

- 1 gram stearyl mercaptan (Preferred quantities)
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 100ml de-ionised water

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 500ml de-ionised water

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid)
- 1000ml de-ionised water.

The solutions were heated to 50°C in an ultrasonic cleaning tank. Samples of polished Argentium Silver were ultrasonically degreased in the solutions for 2 minutes and were rinsed under running tap water. For the first three of the above treatment solutions, it was observed that water was repelled off of the surface leaving the samples dry. Samples treated with the first three solutions above were tarnish tested as described in Example 1 and all showed enhanced tarnish resistance. However, in the case of the samples treated with the last two solutions, water was not repelled off of the surface during the rinsing stage. When the samples dried they showed streaks on the surface which discoloured during the tarnish test. The sample treated with the 500ml solution showed less discolouration than the sample treated with the 1000ml solution. The above experiments show that Argentium silver can be simultaneously degreased and protected against tarnish using a thiol treatment agent applied in an aqueous

system, and that the more concentrated the stearyl mercaptan/EnSolv/detergent/Water solution, the better the tarnish resistance produced.

Example 6

Direct Application - Neat Detergent Solutions (solvent degreased/ aqueous degreased samples)

The following solutions were prepared:

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml detergent (Fairy Liquid) (Preferred quantities)

- 1 gram stearyl mercaptan
- 5 ml EnSolv 765
- 40ml soap (liquid hand soap)

The stearyl mercaptan was initially dissolved into the EnSolv. The detergent was then mixed into the solutions. Samples of Argenium Silver were polished and ultrasonically degreased in EnSolv 765 for 2 minutes. The stearyl mercaptan/EnSolv/detergent solutions were then directly applied to the surface of the Argentium samples using damp cotton wool and massaged into lather. The samples were then rinsed under running tap water. In each case, it was noted that water was repelled off of the polished surface, leaving the samples dry. Samples were tarnish tested as in Example 1 by being exposed to neat ammonium polysulphide solution over a period of 1 hour. They all showed enhanced tarnish resistance. The above direct method for applying the Stearyl Mercaptan was tested on samples degreased in a 2% Fairy Liquid aqueous solution. Enhanced tarnish resistance was again achieved.

Example 7

Cloth Application (solvent degreased samples)

Cloths were prepared by soaking clean cotton cloth in the following solutions:and allowing the cloths to dry

- 0.1 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 0.5 gram Stearyl Mercaptan dissolved in 100ml EnSolv
- 1.0 gram Stearyl Mercaptan dissolved in 100ml EnSolv (Preferred)

Samples of Argentium Silver (which had been polished and ultrasonically degreased in EnSolv 765 for 2 minutes) were wiped with the cloths then buffed with clean cotton wool. Samples were tarnish tested as described in Example 1 by being exposed to ammonium polysulphide solution over a period of 1 hour. All of the samples showed enhanced tarnish resistance.

Example 8

Hexadecyl and octadecyl mercaptan in Fairy liquid

Hexadecyl mercaptan (1g) in the liquid state was mixed with Fairy liquid (surfactant containing anionic and nonionic surface active agents) and with water in the quantities indicated below:

Reference	Fairy liquid (ml)	Deionised water (ml)
8.1	40	Nil
8.2	100	Nil
8.3	200	Nil
8.4	40	100

8.5	40	200

The ingredients of solution 8.2 appeared to mix well without needing the hexadecyl mercaptan to be dissolved in an organic solvent beforehand. A sample of Argentium silver was immersed in the resulting solution for 10 minutes and rinsed. The surface of the Argentium sample had become hydrophobic, suggesting the formation of a layer of hexadecyl mercaptan attached to the surface of the Argentium silver. It rinsed well in water without any noticeable deposit being left on the surface after rinsing. A region of the sample was rubbed with cotton wool soaked in EnSolv 765 and then subjected to tarnish testing with neat ammonium polysulphide over a period of 45 minutes. Excellent tarnish resistance was noted, without significant difference between the region that had been treated with EnSolv 765 and the region that had not been so treated. Similar solutions were prepared from octadecyl mercaptan and Fairy liquid. They were transparent at first, but of lesser stability with separation of a surface layer of octadecyl mercaptan after some months.

Example 9

Hexadecyl mercaptan in Simple shower gel

Hexadecyl mercaptan in the liquid state was mixed with Simple shower gel (a clear shower gel from Accentia Health and Beauty Ltd, Birmingham, UK, and believed to contain sodium laureth sulfate and cocamidopropyl betaine as principal surfactants, together with cocamide DEA and incidental ingredients) and with water in the quantities indicated below:

Reference	HDM (g)	Simple (ml)	Deionised water (ml)
9.1	1	100	Nil
9.2	1	100	100
9.3	5	100	100
9.4	1	200	100

Shortly after mixing, solutions 9.1 and 9.4 were completely transparent viscous gels free from noticeable separation of the hexadecyl mercaptan. Sample 9.2 was also completely transparent but had a water-like consistency and again did not exhibit separation of hexadecyl mercaptan. Sample 9.3 which also had a water-like consistency appeared as a milky emulsion when shaken but exhibited separation of hexadecyl mercaptan at the surface on standing.

In a preliminary experiment, a sample of Argentium silver was immersed in solution 9.1 for 10 minutes and rinsed. The surface of the Argentium sample had become hydrophobic, suggesting the formation of a layer of hexadecyl mercaptan attached to the surface of the Argentium silver. It rinsed well in water without any noticeable deposit being left on the surface after rinsing. When tested with neat ammonium polysulfide, excellent tarnish resistance was noted.

Samples of Argentium silver and conventional Sterling silver were prepared as follows. Each sample was polished with Steelbright polish, followed by rouge, and then ultrasonically degreased for two minutes in a 2 wt% Fairy Liquid solution in water at 54°C. It was then further degreased for 5 minutes in ethanol and immersed at ambient temperatures in the test solution. After removal, part of each sample was rubbed with tissue soaked in EnSolv 765 and then subjected to tarnish testing with neat ammonium polysulphide over a period of 45 minutes. Argentium samples showed excellent tarnish resistance and thiol bonding, especially good results being obtained with solutions 9.1 and 9.4 compared to the higher water content solutions 9.2 and 9.3. Solutions 9.1 and 9.4 appeared to provide some tarnish protection for standard Sterling silver also, but

the thiol layer could be removed easily as was apparent from the differences between the untreated and the EnSolv 765 treated regions.

Example 10

Mixtures of cocamidopropyl betaine (CPB) and sodium laureth sulfate (SLS)

The above materials were supplied as a thick pourable aqueous liquid and as a highly concentrated somewhat gelatinous liquid (70% active) by Surfachem Ltd of Leeds, United Kindgom. Hexadecyl mercaptan (1 ml) in the liquid state was mixed with these materials in the quantities indicated below:

Reference	SLS (ml)	CPB (ml)	Water (ml)
10.1	40	40	100
10.2	40	20	100
10.3	30	10	100
10.4	10	30	50
10.5	30	10	160

For solution 10.1, hexadecyl mercaptan was added to a thick mixture of sodium laureth sulphate and cocamidopropyl betaine after which water was added and the solution was mixed cold. The resulting mixture initially had a thick foamy-white texture which on settling turned into a transparent gel. Solution 10.2 was somewhat similar. Solution 10.3 was watery and was initially slightly transparent with lots of bubbles on top of the solution., and on settling overnight it became transparent. Solution 10.4 was mixed with gentle heating to about 35°C Heat appeared to slightly help with the mixing procedure. After a few minutes of mixing the mixture foamed severely. The mixture was allowed to stand overnight and formed a viscous solution. Solution 10.5 was heated to approximately 35°C whilst mixing. Water was last ingredient to be added. Using heat for mixing

proved beneficial. The solution appeared very foamy but this settled over a few hours (within 12 hours) to form a transparent solution slightly thicker than water.

Argentium silver samples were prepared by polishing in Steelbright and then rouge, ultrasonically degreasing in a 2% aqueous Fairy Liquid solution further degreasing in acetone, immersion in the test solution at ambient temperatures for 10 minutes, and washing under cold running tap water. A lower region of each sample was rubbed with tissue soaked in EnSolv in an attempt to attempt to remove any thiols, after which the sample was left to stand for 45 minutes and were then exposed to a neat ammonium polysuphide accelerated tarnishing test for 45 minnutes.

All the samples showed extremely good hydrophobic properties during the rinsing process which indicates presence of thiols. Water drops were repelled and there was no need to dry each sample. The samples performed well in the tarnishing test with resistance to tarnishing and little difference between the rubbed and un-rubbed regions. It was concluded that the hexadecyl mecaptan in each sample tested had created a tarnish-protective thiol-bonded layer on the surface of the Argentium silver.